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研究課題名(和文) Study of group-IVB metal doped BiVO<sub>4</sub> thin-films for development of a highly efficient Z-Scheme photocatalyst研究課題名(英文) Study of group-IVB metal doped BiVO<sub>4</sub> thin-films for development of a highly efficient Z-Scheme photocatalyst

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研究成果の概要(和文)：将来のエネルギー源として期待される水素の生成を目指し、BiVO<sub>4</sub> 酸素(O<sub>2</sub>)発生光触媒の研究を行ってきました。特に、光学特性、結晶構造、および光触媒性能に対する、BiVO<sub>4</sub> 材料へのジルコニウム(Zr)のドーピングの影響を研究しました。n型伝導性を高めるBiVO<sub>4</sub>のBiサイトにZrが置換されていることを確認しています。BiVO<sub>4</sub>中のZrの最適化されたドーピングは、Moドーブサンプルと比較してより多くのO<sub>2</sub>を生成することにより、より良いパフォーマンスをもたらします。さらに、スパッタリング法を使用して、ZrドーブBiVO<sub>4</sub>薄膜を作製することに成功しました。

研究成果の学術的意義や社会的意義

Understanding of doping mechanism of Zr in BiVO<sub>4</sub> has academic interest for the enhancement of photo-catalytic performance. Development of BiVO<sub>4</sub> photocatalyst will pave way to reduce dependence of carbon-di-oxide-emitting fossil fuels, and open path for the establishment of hydrogen society.

研究成果の概要(英文)：We have studied BiVO<sub>4</sub> oxygen (O<sub>2</sub>) evolution photocatalyst in aiming for the production of hydrogen, which is considered as future source of energy. In particular we have studied effect of zirconium (Zr), molybdenum (Mo) and titanium doping in BiVO<sub>4</sub> materials on the optical properties, crystal structure and photocatalytic performance. We have confirmed that Zr is substituted on Bi site in BiVO<sub>4</sub> enhancing n-type conductivity. Optimized doping of Zr in BiVO<sub>4</sub> results in better performance by generating more O<sub>2</sub> comparing to Mo-doped samples. In addition, We have confirmed and made a model for the recombination mechanism in the BiVO<sub>4</sub> crystals. Furthermore, we have successfully used sputtering methods to fabricate Zr and Mo-doped BiVO<sub>4</sub> thin films from a single BiVO<sub>4</sub> target. Thus scalable production of BiVO<sub>4</sub> in industry level should be possible for photocatalytic application.

研究分野：Energy Materials and devices, Defect Study

キーワード：Photocatalyst oxygen evolution Hydrogen society Photocarrier dynamics zirconium doping Defect study

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### 1. 研究開始当初の背景

Bismuth vanadate ( $\text{BiVO}_4$ ), an *n*-type metal oxide semiconductor is a potential photoanode for oxygen ( $\text{O}_2$ ) production through water splitting due to its suitable band-gap of  $\sim 2.4$  eV. However, actual solar-to-hydrogen (STH) conversion of  $\text{BiVO}_4$  is below the theoretical limit. This is mainly due to recombination losses, poor electron transport properties, and slow hole transfer kinetics in this material, which result in lower extraction of photo-generated electron-hole pairs in the  $\text{BiVO}_4$  based system. Doping with group IV element, *e.g.*, with zirconium (Zr), thereby, enhancing conductivity are among some options to enhance performance.

### 2. 研究の目的

In our study we aim to understand photocarrier dynamics and recombination mechanism in  **$\text{BiVO}_4$  (BVO)**. We also have investigated the doping mechanism of Zr in  $\text{BiVO}_4$  host crystals as well as mechanism of how Zr enhance photocatalytic activities in BVO. Results were compared with other dopant like molybdenum (Mo). In addition, to reduce photo corrosion, and also to make hetero structure, we have fabricated vacuum deposited BVO in thin films doped with Zr. Finally, to complete Z-scheme photocatalyst structure with BVO we also deposited suitable p-type thin films like  $\text{Cu(In,Ga)Se}_2$ .

### 3. 研究の方法

BVO powders were prepared via liquid–solid reaction, whereas BVO thin films were deposited through electrodeposition as well as sputtering methods. Crystal structure was studied by x-ray diffraction method (XRD). Photo-carrier recombination in BVO was studied using steady-state photoluminescence (PL) and time-resolved photoluminescence measurements (TRPL) using a femtosecond Ti: sapphire laser with 400 nm of wavelength in continuous wave and pulsed wave with width of  $\sim 80$  fs, respectively. X-ray absorption spectra (XANES) around the Zr K-edge ( $\sim 17,998$  eV) and extended X-ray absorption fine structure (EXAFS) were conducted using at 12C beamline at Photon Factory (PF) in Tsukuba, Japan.

### 4. 研究成果

a) **Photocatalytic activity of Zr doped and Undoped BVO:** Photocatalytic activity increases with an increase of Zr doping level until an optimum amount of 0.1 mol.% keeping the monoclinic crystal structure as observed from XRD. Higher Zr doping beyond 0.1 mol.% deteriorate the activity, mainly due to phase transition to the tetragonal structure [1,2].

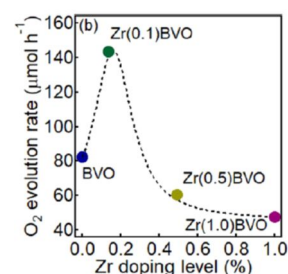


Fig. 1. Photocatalytic  $\text{O}_2$  evolution of undoped and Zr doped BVO with different dopant level in mol% inside parenthesis.

### b) Photocarrier recombination in BVO:

Carrier recombination dynamics in BVO was investigated using temperature-dependent, steady-state, and time-resolved PL. We developed a model showing that radiative recombination in BVO occurs through donor-to-acceptor transition (DAP), associated with shallow acceptor levels around 35 and 115 meV, above the valence band, and donor levels around 655 and 575 below the conduction band. Effective lifetimes ( $\tau$ ) of minority carrier were found in the

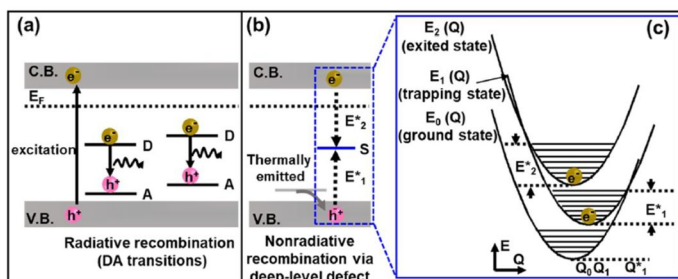


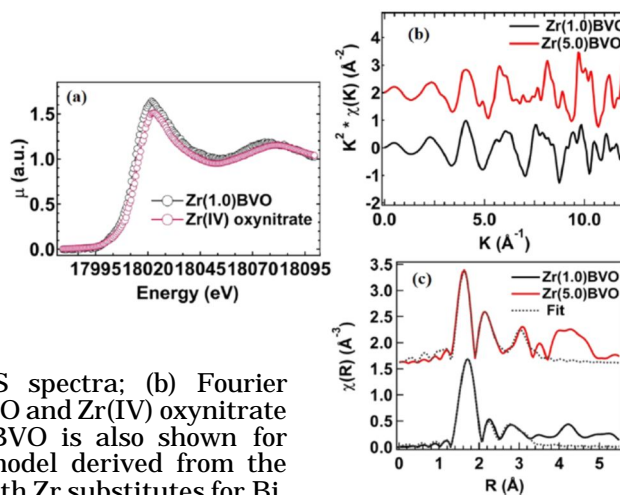
Fig. 2. Photocarrier dynamics in BVO. (a) The radiative recombination via DAP, (b) Thermal quenching of PL due to escape of holes from the shallow acceptor-levels, (c) Configuration Coordinate diagram showing capture process of the photocarrier by a deep-level defect.

order of nanoseconds, which is far behind the ideal radiative lifetime of 6  $\mu$ s, calculated theoretically. This phenomenon suggests that the photocarrier recombination in BVO occurs predominantly through multiphonon nonradiative recombination, via deep level defects [3].

### c) Mechanism of Zr incorporation in

#### BVO host crystal:

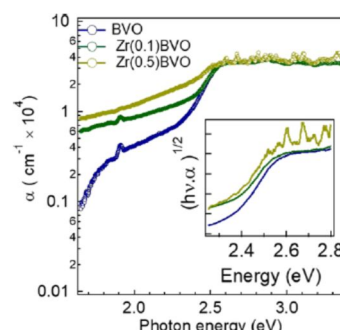
Extended X-ray absorption fine structure (EXAFS) along with X-ray absorption near edge structure (XANES) at Fig. 3 suggests that Zr is incorporated as a substitute on Bi site in BVO enhancing n-type conductivity (until optimum amount of 0.1 mol. %) [1].



**Fig. 3.** (right): (a) Zr k-edge XANES spectra; (b) Fourier transformed  $K^2$  Zr EXAFS of Zr(1.0)BVO and Zr(IV) oxynitrate reference samples. EXAFS of Zr(5.0)BVO is also shown for comparison. The data were fit to a model derived from the monoclinic scheelite structure of BVO with Zr substitutes for Bi.

### d) Effect of Zr on the photoexcited carrier recombination in BVO:

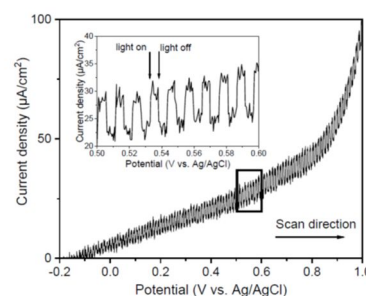
Although incorporation of optimum amount of Zr at Bi-sites in improved activity, due to ionic radius difference, Zr incorporation causes local distortion, leading to large formation of  $O_{vac}$  and possibly ZrBi- $O_{vac}$  defect complexes low donor efficiency (self compensation), increased nonradiative recombination and small hole diffusion length. Sub-gap absorption in the Fig. 4 is associated with Zr-oxygen vacancy defect complexes [1].



**Fig. 4.:** Absorption coefficients as functions of incident photon energy for undoped BVO and Zr(0.1)BVO powders, calculated from reflectance and transmittance measurements. The inset is Tauc plot derived from absorption spectra.

### e) Sputtering of BVO from single target:

We have done Monte Carlo simulation to study effect of RF Power on the ratio of Bi and V in  $BiVO_4$  Films sputtered from single target. BVO films with monoclinic scheelite crystal structures were obtained at high RF power and found to exhibit comparable photocatalytic performances as shown in Fig. 5 [4].



**Fig. 5.** Chopped LSV of BVO film deposited on FTO at 200 W in an electrolyte containing 0.02 mol/L  $Na_2S$  and 0.02 mol/L  $Na_2SO_3$  hole scavengers under simulated sunlight (AM 1.5G).

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5. 主な発表論文等

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オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する
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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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